Gulf General Atomic
Incorporated
P. O. Box 608, San Diego, California 92112

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ABSTRACT

The transport rates of fuel components from 90UC-10ZrC, UO_2 and W-60 vol% UO_2 cermet through chemically vapor-deposited fluoride tungsten cladding were determined in the temperature range 1923-2273°K, using samples of both planar and cylindrical configurations. From the results obtained, it is estimated that the total amount of uranium transported through 40 mil thick fluoride tungsten cladding in 10,000 hours may vary from a few to 5000 monolayers, depending upon fuel composition, fuel stoichiometry and temperature. The uranium transport rate of UO_2 through fluoride tungsten cladding at 2273°K is many orders of magnitude higher than that reported for powder metallurgy or arc-cast tungsten cladding at the same temperature, implying the importance of cladding structure to uranium transport rate. It is shown that the carbon transport through fluoride tungsten cladding will not cause a significant change in fuel stoichiometry at 2073°K in 10,000 hours.

Measurements were made on the fission product recoil range and the diffusion constants of various fission products in fluoride tungsten. On the basis of the results obtained and an equation derived for the transport rates of primary fission products from fuels through cladding by both the recoil and the dissolution mechanisms, the total accumulations of various primary fission products outside the cladding were calculated as a function of time and temperature. It is shown that among the fission products studied the Ru isotopes constitute the major components of those diffusing through the cladding. Post-irradiation annealing studies substantiated this finding and showed that no significant transport of Xe^{133} through 20 mil thick fluoride tungsten cladding at 2073°K in 1000 hours.

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INTRODUCTION

The work function of a thermionic emitter surface is sensitive to the presence of a fraction of a monolayer of adsorbed impurity atoms. In a nuclear thermionic converter, the emitter consists of a refractory metal cladding in close contact with nuclear fuel materials at high temperatures in a neutron environment. If the transport rates of fuel components and fission products through the cladding are rapid, they may accumulate on the electrode surfaces and affect the thermal and electrical performance of the converter. To gain an insight of the problem involved, experimental measurements were made on the transport rates of fuel components through fluoride tungsten claddings of planar emitters fueled with 90UC-10ZrC and UO_2 and of cylindrical emitters fueled with 90UC-10ZrC and W-60 vol% UO_2 cermet. In addition, the fission recoil ranges and the diffusion constants of various fission products in fluoride tungsten were determined, from which their transport rates through fluoride tungsten claddings were deduced and compared with results obtained from post irradiation annealing studies made on planar emitters fueled with 90UC-10ZrC and UO_2.

EXPERIMENTAL AND ANALYTICAL METHODS

1. Fuel Component Transport

Fuel component transport data were obtained by using both planar and cylindrical samples. The planar samples consisted of 90UC-10ZrC or UO_2 wafers of 20 to 40 mil thickness of 0.250 to 0.375 inch diameter clad with fluoride tungsten of 20 or 40 mil thickness. Each sample was heated at a certain temperature for a given period of time in vacuum by electron bombarding one of its flat surfaces. The uranium diffusing through the other flat surface was gathered on a water-cooled stainless steel collector and its amount determined by dissolving the deposit in dilute HNO_3, irradiating the solution in Gulf General Atomic's TRIGA reactor at 250 kw for 1 hour, and counting the activity of the I^{134} formed. In some cases, the carbon content in the deposit was measured by oxidizing it to CO_2 with oxygen and Cu_2O at about 400°C and determining the amount of CO_2 formed

by gas chromatographic techniques. The cylindrical samples consisted of 90UC-10ZrC and W-60 vol% UO_2 cermet fueled emitters in out-of-pile cylindrical converters which were life tested for periods from a few thousands to ten thousand hours. The uranium content in the deposit condensed on the collector surface was determined by the same radiochemical method described above.

2. Fission Product Transport

(1) Determination of fission product recoil range in fluoride tungsten.

Polished surfaces (to 0000 emery paper) of vacuum annealed (2073°K, 50 hours) fluoride tungsten discs 0.375 inch in diameter and 20 mil in thickness, were held in contact with a U^{235} source and irradiated in Gulf General Atomic's TRIGA reactor at ambient temperature at 250 kw for 1/2 hour. Thin layers were removed from the fission product impregnated surfaces either by mechanical polishing or by electrolytic dissolution. The concentrations of the fission products La^{140}, Ru^{103} and Zr^{95}-Nb^{95} in each layer were determined by radioactive counting techniques, and the thickness of each layer removed was determined by weighing. The recoil range of each of these fission product studied was deduced from its activity distribution in each tungsten disc.

(2) Determination of diffusion constants of fission products in fluoride tungsten.

The diffusion constants of Ru^{103}, Ce^{141}, Zr^{95}, Ba^{140}, I^{131} and Te^{132} in fluoride tungsten were determined in the temperature range 1873° to 2123°K by the diffusion couple method. Each couple consisted of two fluoride tungsten discs 0.375 inch in diameter and 20 mils in thickness, each with one of its two flat surfaces prepared and impregnated with fission products according to the method described above. The impregnated discs were diffusion bonded in a vacuum hot press at the planned diffusion temperature and 5000 psi for 3 hours with the impregnated surfaces facing each other. The diffusion bonded couple was annealed in a tantalum resistance furnace

in vacuum at the desired temperature. After the diffusion anneal, the sample was mounted in plastic and sectioned by anoidic dissolution in 10% NaOH solutions from one tungsten disc to the other tungsten disc across the interface. The Ru^{103}, Ce^{141}, Zr^{95}, Ba^{140}, I^{131} and Te^{132} contents of the solutions obtained were determined by radiochemical techniques. The thicknesses of the tungsten layers dissolved were evaluated from the tungsten contents of these solutions. Since the initial fission product sources extend to a distance of only 5 to 6 microns (see the results on fission recoil range in tungsten below) at either side of the interface of the diffusion couple, the configuration of the sample can be treated as that of an infinite system containing an infinitely thin plane source at the interface,[1] provided the diffusion-anneal time is long enough to produce a diffusion distance much greater than 5 to 6 microns. For such a system, a straight line should result if log C if plotted against X^2, when C is the concentration of the fission product at a distance X cm. from the interface. The diffusion constant D (in cm^2/sec) can be evaluated from the slope of such a straight line, which is equal to $\frac{1}{4Dt}$; where t is the diffusion time in seconds.

(3) Calculation of fission product transport through cladding from fission recoil range and diffusion constant.

A general equation was derived[2] for a planar fuel-clad configuration to relate the transport rates of primary fission products (i.e. fission products formed either directly by the fission of U^{235} or from precursors of very short half-lives) through the cladding as a function of time during their continuous generation in the fuel material by taking into account the entry of the fission products into the cladding by both the recoil and the dissolution mechanism. The assumption was made that the diffusion of fission products from the fuel is such that a homogeneous concentration distribution in the fuel is maintained at all times. The equation is shown below together with the nomenclature of the symbols used (Table 1).

$$R(t) = R - \left\{ \frac{2D}{(b-a)^2} \sum_{n=1}^{\infty} \alpha_n \exp - \left[\left(\lambda + \frac{D\alpha_n^2}{(b-a)^2} \right) \right] t \right\} \times$$

$$\left\{ \frac{(b-a)\, S_1 + \frac{A(b-a)}{\delta_2} \left[-\phi\, \delta_2 + \frac{\beta(b-a)^2}{\alpha_n^2} - \frac{\beta(b-a)^2}{\alpha_n^2} \cos \frac{\delta_2 \alpha_n}{b-a} + \frac{\phi(b-a)}{\alpha_n} \sin \frac{\alpha_n \delta_2}{b-a} \right]}{\left[\lambda + \frac{D\alpha_n^2}{(b-a)^2} \right] \left\{ \left[\beta_1 (b-a) + \phi \right] \sin \alpha_n + \phi\, \alpha_n \cos \alpha_n \right\}} \right\} \tag{1}$$

where

$$R = \left\{ \frac{S_1 + \frac{A}{\delta_2} \left[-\phi\, \delta_2 + \phi \sqrt{\frac{D}{\lambda}} \sinh \sqrt{\frac{\lambda}{D}}\, \delta_2 + \beta \frac{D}{\lambda} \cosh \sqrt{\frac{\lambda}{D}}\, \delta_2 - \beta \frac{D}{\lambda} \right]}{\beta \cosh \sqrt{\frac{\lambda}{D}} (b-a) + \phi \sqrt{\frac{\lambda}{D}} \sinh \sqrt{\frac{\lambda}{D}} (b-a)} \right\} \tag{2}$$

The total accumulation of a given fission product outside the cladding at time equal to t_f is

$$M(t_f) = \int_0^{t_f} R(t) \left[\exp - \lambda (t_f - t) \right] dt \quad \text{atom/cm}^2 \tag{3}$$

(4) Post-irradiation annealing studies of fission product transport through fluoride tungsten cladding.

Fluoride tungsten clad (20 mil thick) 90UC-10ZrC and UO_2 wafers of 5% enrichment were irradiated in Gulf General Atomic's TRIGA reactor at ambient temperature to attain a total of 1×10^{14} fissions in each fuel wafer. Each irradiated sample was heated in vacuum at 2073°K for 1000 hours in water-cooled stainless steel enclosure connected to a liquid nitrogen cooled charcoal trap. Any Xe^{133} diffusing through the cladding was collected in the trap and its activity in the trap was counted every few hours. The condensable fission products diffusing through the cladding were collected on the surface of a water-cooled stainless steel collector. The collector deposit was dissolved in dilute HNO_3 at the end of the experiment and the solution obtained was analyzed radiochemically for the total transport of various fission products through the cladding at 2073°K in 1000 hours.

Table 1

NOMENCLATURE OF SYMBOLS USED IN EQUATIONS (1) AND (2)

Symbol	Definition
$R(t)$	Fission product release rate from the outer surface of cladding at time t (atoms/cm^2-sec)
R	Fission product release rate from the outer surface of cladding at steady state condition, i.e., when the rate of fission product injection into the cladding is balanced by the rate of decay plus the rate of release (atoms/cm^2-sec)
D	Diffusion constant of fission product in fluoride tungsten (cm^2/sec)
b	Distance between the outer surface of the cladding and the center of the fuel body (cm)
a	Distance between the fuel-clad interface and the center of the fuel body (cm)
(b-a)	Thickness of cladding (cm)
α_n	Roots of the transcendental equation $\cot \alpha_n = [\phi/\beta(b-a)]\ \alpha_n$
ϕ	Ratio of fission product concentration in fuel to fission product concentration in clad at fuel-clad interface
β	Fuel-clad interfacial area per unit fuel volume (cm^2/cc)
λ	Disintegration constant of fission product (sec^{-1})
t	Time of diffusion (sec)
δ_1	Recoil range of fission product in fuel material (cm)
δ_2	Recoil range of fission product in tungsten cladding (cm)
S_1	Rate of increase of fission product source concentration in the fuel during the operation of the fuel element (atoms/cc-sec) = $Q - (\beta/4)\delta_1 Q$, where Q = rate of generation of fission product atoms in unit volume of fuel = 3×10^{10} PY (P = fission power in watts/cc and Y = fission yield), and $(\beta/4)\delta_1 Q$ = rate of loss of fission product atoms per unit volume of fuel due to fission recoil into tungsten cladding

Table I (Continued)

NOMENCLATURE OF SYMBOLS USED IN EQUATIONS (1) AND (2)

Symbol	Definition
A	Rate of increase of fission product concentration in tungsten cladding at the fuel-clad interface due to fission recoil (atoms/cc-sec) = $1/2\ Q(\delta_1/\delta_2)$, since the total number of atoms of fission product recoiled into the cladding is $1/4\ (Q\ \delta_1)$ and this total number is distributed linearly in a zone of width equal to δ_2 in the cladding.

RESULTS AND CONCLUSIONS

1. Fuel Component Transport

The results are summarized in Table 2. In Fig. 1 the uranium fluxes shown in Table 2 for the various fuel materials are plotted as number of monolayer (each monolayer $\approx 5 \times 10^{14}$ atoms/cm^2) transported through 40 mil thick fluoride tungsten cladding in 10,000 hours as a function of cladding temperature, assuming that the uranium transport is inversely proportional to cladding thickness and directly proportional to time. The results obtained by Kaznoff and Sanderson[3] on uranium transport rates from $UO_{2.004}$ through fluoride tungsten, powder metallurgy tungsten and arc-cast tungsten are included for comparison.

From the results shown in Table 2 and Fig. 1, the following conclusions can be drawn.

(1) The uranium transport rate is affected by fuel composition and fuel stoichiometry. The transport rate from the oxide fuel, especially the cermet fuel, is less than that from the carbide fuel at equal temperature. For the carbide fuels studied, the carbon rich fuel has a lower uranium transport rate than the stoichiometric fuel, presumably due to the lower uranium activity of the carbon rich fuel.

Table 2

FUEL COMPONENT TRANSPORT RATES THROUGH FLUORIDE TUNGSTEN

Sample No.	Fuel	Cladding Thickness (mil)	Sample Configuration	Temperature (°K)	Time (hr)	Average Uranium Flux (gm/cm^2, hr)	Average Carbon Flux (gm/cm^2, hr)
1	$UO_{2.004}$	20	Planar	2273	1005	1.1×10^{-7}	
2	$UO_{0.90}Zr_{0.10}C_{1.02}$	20	Planar	2223	820	2.5×10^{-7}	
3		20	Planar	2173	1000	1.4×10^{-7}	
4		40	Planar	2073	10146	1.2×10^{-8}	1.6×10^{-9}
5		40	Planar	2073	10000	1.1×10^{-8}	1.8×10^{-9}
6	$U_{0.90}Zr_{0.10}C_{1.00}$	40	Cylindrical	2023	7558	6.0×10^{-8}	
7	W-60 vol% UO_2	40	Cylindrical	2023	10406	3.6×10^{-10}	
8		40	Cylindrical	1923	3235	6.0×10^{-11}	

(2) At the normal emitter operating temperatures (1973-2073°K), the uranium transports through 40 mil thick fluoride tungsten cladding vary from about 5 to 500 monolayers in 10,000 hours for the various fuel materials studied. Whether such uranium transports would change the electrical and thermal performance of the electrodes in a thermionic converter depends upon the rate of evaporation of uranium from the emitter surface and the rate of diffusion of uranium into the collector bulk. These rates are affected by electrode temperature, nature of electrode material and the presence of other fuel components. One of the main objectives for testing fueled converters is to map out the operating conditions under which the converter performance is least affected by such finite rates of uranium transport.

(3) The uranium transport rate through tungsten cladding is a strong function of the structure of the cladding. Transport rates through the equiaxial grains of powder metallurgy or arc-cast tungsten are much lower than that through the columnar grains of fluoride tungsten, as pointed out previously by Kaznoff and Sanderson.[3]

(4) Although the carbon transport rate from the carbide fuel through the fluoride tungsten cladding is measurable, its effect on fuel stoichiometry is small. For instance, assuming the carbide contains 5 wt% carbon and has a density of 10 gm/c.c., for an emitter of 1/2 inch diameter and 40 mil cladding thickness, only 0.017% of the carbon content of the carbide fuel is lost in 10,000 hours by diffusion through the cladding.

2. Fission Product Transport

(1) Fission recoil ranges.

Studies were made on a total of six samples. The average values for fission fragments of mass 140, mass 103 and mass 95 are 5.2, 5.4 and 5.6 microns respectively.

(2) Diffusion Constants.

Studies were carried out at 1873°, 1973°, 2023°, and 2123°K respectively. The variation of the diffusion constant D with temperature is expressed in the form $D = D_o \exp\left[\frac{-Q}{RT}\right]$, with the D_o and the Q values for the various fission products studied shown in Table 3.

Table 3

RESULTS FOR THE DIFFUSION OF FISSION PRODUCTS IN FLUORIDE TUNGSTEN

Isotope	D_o (cm^2/sec)	Q (cal./mole)
Ru^{103}	5.70×10^{-2}	41000
Ce^{141}	1.02×10^{-2}	39600
Zr^{95}	9.25×10^{-3}	39400
Ba^{140}	4.15×10^{-1}	49100
I^{131}	4.25×10^{-1}	49600
Te^{132}	3.36×10^{-1}	49400

The metallic fission products studied have D values higher than that of the non-metallic fission products studied and Ru has the highest D value.

(3) Analytical evaluation of fission product transport through fluoride tungsten cladding.

A computer program was devised for the evaluation of the rate of transport R(t) and the total accumulation M(t) outside the cladding as a function of time according to Equations (1) and 3), using the fission recoil ranges and diffusion constants given above. Figure 2 shows the results on M(t) values as a function of time at a cladding temperature of 2073°K for both the radioactive and the stable Ru, Zr, Ce, Ba, I and Te primary fission product isotopes,

assuming (b-a) = 0.1 cm, P = 500 watt/cc, $\beta = 4$ cm^2/cc, $\delta_1 = 6 \times 10^{-4}$ cm. $\phi = 1$ for the Ru, Ba, I and Te isotopes, and $\phi = 100$ for the Zr and Ce isotopes which form stable carbides and oxides. For the Ru isotopes, the calculations were extended to 1973°K and 1873°K and the results are shown in Fig. 3. It can be seen that Ru isotopes consitute the major components of fission products transported through the cladding. The total amount of Ru isotopes transported through the cladding in 10,000 hours is about 1000 monolayers at 2073°K, which decreases to about 100 monolayers at 1973°K and to about a few monolayers at 1873°K. Thus the Ru isotope transport is of the same order of magnitude as the uranium transport from a carbide fuel at the same temperature. It must be pointed out, however, that these calculations were made by assuming that the rates of diffusion of these fission products in the fuel material are not the limiting factor for the transport process through the cladding. In the event this is not true, then the observed transport should be less than that shown in Figs. 2 and 3.

(4) Post-irradiation annealing studies of fission product transport through fluoride tungsten cladding.

Two samples containing $U_{0.90}$ $Zr_{0.10}$ $C_{1.02}$ fuel wafers and two samples containing $UO_{2.005}$ fuel wafers were studied at 2073°K for 1000 hours, using the experimental method described above. In each case no Xe^{133} transport through the cladding was observed beyond the experimental detection limit (~ 10^7 atoms), and Ru^{103} was the only radioactive fission product detected on the collector surface in amounts corresponding to 0.03% of the initial Ru^{103} contents of the carbide fuel and 0.18% of the initial Ru^{103} contents of the oxide fuel. Thus the results on Ru^{103} transport confirm the conclusion reached in the analytical evaluation made by using the measured fission recoil ranges and diffusion constants.

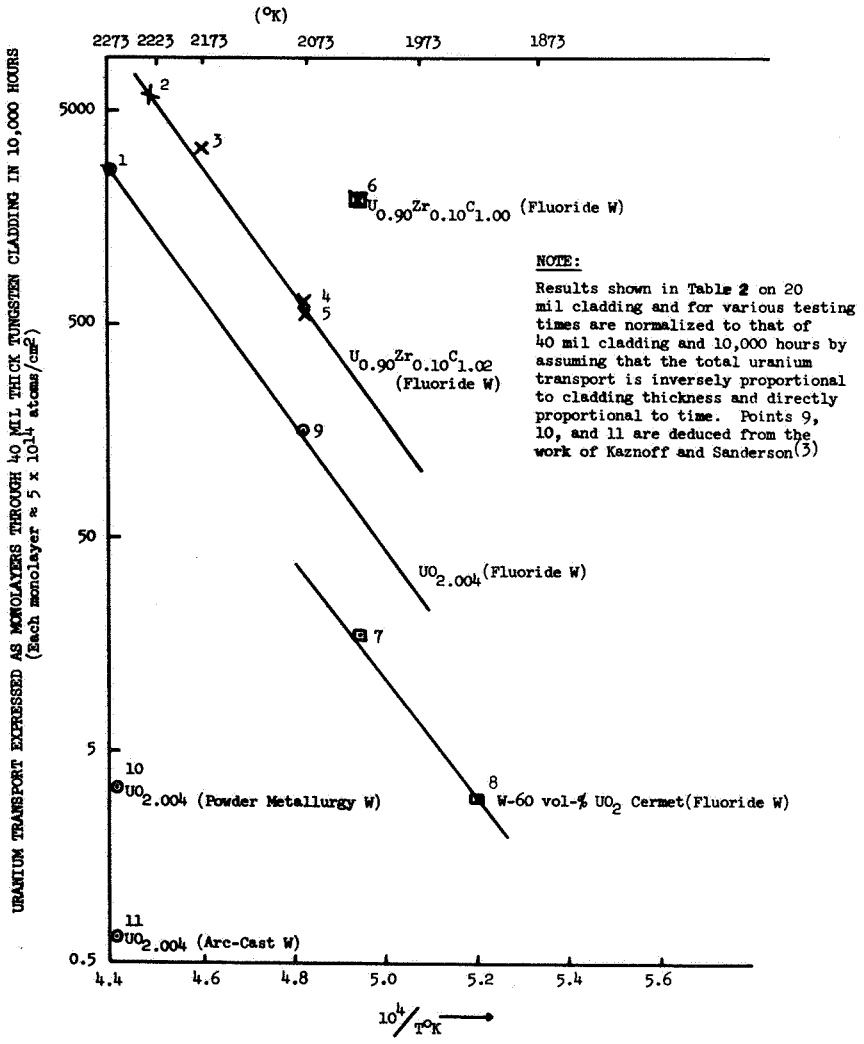

Fig. 1--(U) Uranium transport through 40 mil thick tungsten cladding in 10,000 hours at various temperatures

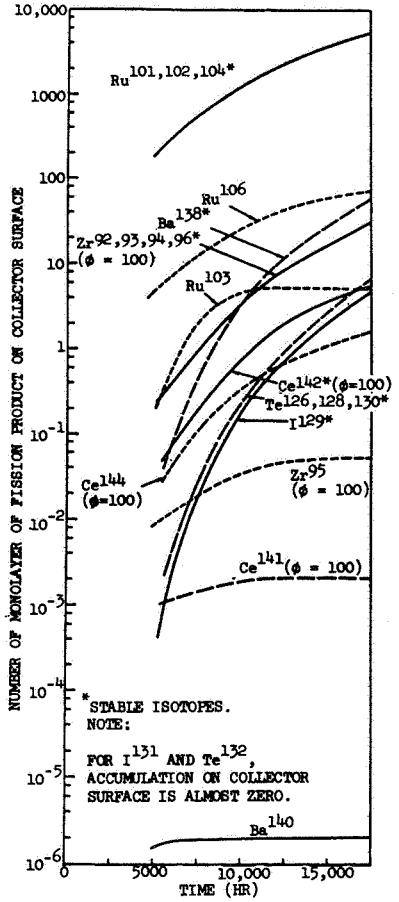

Fig. 2--(U) Number of monolayers of various fission product isotope accumulation on collector surface as a function of time. Temperature of tungsten cladding = 2073°K (assume 1 monolayer ~5 x 10^{14} atoms/cm^2)

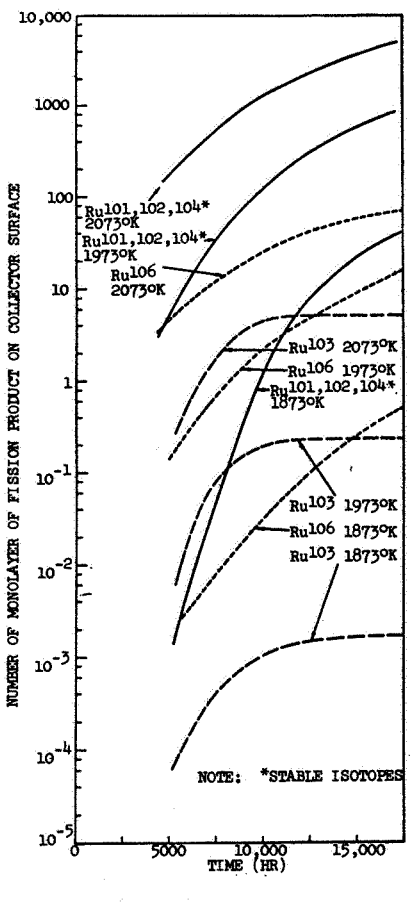

Fig. 3--(U) Number of monolayers of various Ru fission product isotope accumulation on collector surface as a function of tungsten cladding temperature and time (Assume 1 monolayer ~5 x 10^{14} atoms/cm^2)

REFERENCES

(1) "Diffusion in Solids, Liquids, Gases," p. 17, W. Jost, Academic Press Inc., New York, (1952).

(2) Private Communication with B. W. Roos of Gulf General Atomic.

(3) KAZNOFF, A. I., and M. J. SANDERSON, "Diffusion and Interactions in the Urania-Tungsten and Urania-Molybdenum Systems." International Conference on Thermionic Electrical Power Generation, London, (September 20-24, 1965).

FIGURES

1. Uranium transport through 40 mil thick tungsten cladding in 10,000 hours at various temperatures.

2. Number of monolayers of various fission product isotope accumulation on collector surface as a function of time. Temperature of tungsten cladding = 2073°K (assume 1 monolayer ~5 x 10^{14} atoms/cm^2).

3. Number of monolayers of various Ru fission product isotope accumulation on collector surface as a function of tungsten cladding temperature and time (assume 1 monolayer ~5 x 10^{14} atoms/cm^2).